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研究課題名（和文）ホスト-ゲスト電荷移動によるガス応答性多孔質磁石の開発

研究課題名（英文）Development of Gas-Responsive Porous Magnets via Host-Guest Charge Transfer

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交付決定額（研究期間全体）：（直接経費）　　3,300,000円

研究成果の概要（和文）：ホスト－ゲスト間電子移動の制御によるり反強磁性体と常磁性体間を繰り返し変換なゲスト応答性多孔質磁石の開発に成功しました。
1．層状多孔質磁石は、ヨウ素を吸着する前は、反強磁性体であり、広義の磁気秩序を持つ状態（磁石 ON の状態）です（相転移温度TN = 90 K）。2．この多孔質磁石にヨウ素を吸着させると、常磁性体（磁石 OFF の状態）になります。ヨウ素分子を除去すれば元の反強磁性体へと戻ります。3．この機構は、吸着されたヨウ素分子が分子骨格から電子を受け取り、分子骨格の電子状態を変化させることに因ります。

研究成果の学術的意義や社会的意義
「多孔質磁石」は、従来からよく知られた電場・磁場・光・圧力などの物理的な刺激とは異なり、「分子吸脱着」という化学的な刺激により駆動する材料です。本研究における、吸着分子とホスト骨格の間での直接的な電子授受により駆動する可逆磁気相変換は世界初観測であり、新たな駆動原理により「化学物質による物性制御」を実現したという点で、高機能分子デバイスの実現へ向けて、基礎・応用の両面から大変意義深い結果だと考えられます。このような材料は、化学的刺激により駆動する分子デバイスの新たな駆動原理の一つとして今後の発展が期待できます。

研究成果の概要（英文）：We demonstrated a guest-responsive porous magnet that is a paramagnet on I2 adsorption (with its magnetism ‘switched off’) and converts into a antiferromagnt on I2 desorption (with its magnetism now ‘switched on’) via host−guest electron transfer.

研究分野：無機・錯体化学

キーワード：Porous magnet　Host-guest chemistry　Electron transfer　Charge transfer　Magnetic property　Electrical property

１．研究開始当初の背景

Growing demands for multiple and smart sensors in the age of the Internet of Things (IoT) have boosted the development of multifunctional materials, which provide tunable physical properties in response to the environment surrounding us such as electric field, magnetic field, light, temperature, and guest. Porous magnets that combine porosity and magnetic ordering offer the opportunity to control magnetism by guest molecules. [1] Nevertheless, the magnetic ordering and porosity are always the irreconcilable contradictions in a single material, as shorter organic linkers are generally associated with stronger magnetic coupling but consequently smaller porosity. The reversible magnetic change in porous magnets caused by guest accommodation has so far been observed via 1) structural modification, [2-3] 2) spin meditation of oxygen, [4] and 3) electronic state modulation. [5-6] These provide versatile approaches to achieve switchable magnetic change. If the guest directly interacted with the host framework via the charge transfer, it may fundamentally produce a huge magnetic change. From this perspective, we herein propose a proof-of-concept study, i.e. host−guest charge transfer (HGCT), utilizing electron−acceptor guest accommodation (e.g. O_2, NO, I_2) to achieve reversible magnetic phase switch in magnetic metal−organic frameworks (MOFs) (Figure 1). The proposed HGCT strategy will not only pave a new path toward the development of magnetic phase-switchable porous magnets but also bring prosperous applications as the gas sensor or memory storage.

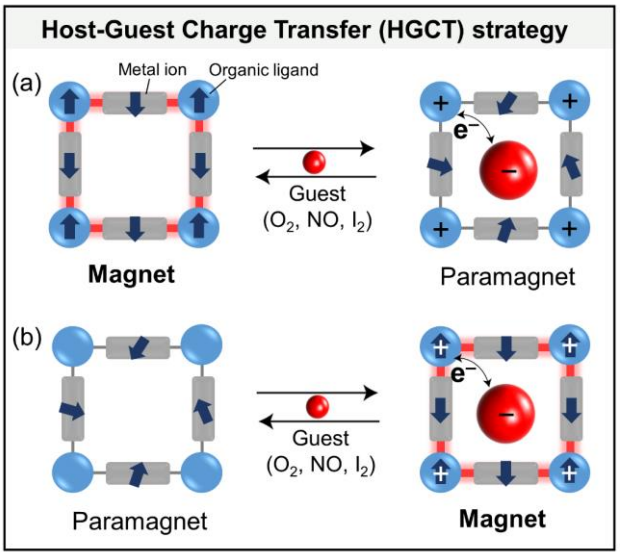

Figure 1. Schematics of host-guest charge transfer strategy towards the control of magnetism in magnetic metal−organic frameworks.

２．研究の目的

The objective of this proposal aims to propose a new HGCT strategy to fundamentally realize a large magnetic change in magnetic MOFs by electron−acceptor gas. To realize the HGCT may rely on 1) the formation of strong host−guest interaction (e.g. cooperative bonding or charge transfer) and 2) electron−acceptor guest (e.g. O_2, NO, I_2). This project, which involves the use of HGCT for magnetic change, has the potential to achieve magnetic phase switches and enable the development of a new form of porous magnets. Despite the fact that the HGCT has been widely employed to regulate various functions for selective sorption, electrical conductivity, luminescence, and spin state, a change in the magnetic phase, has, surprisingly, never been reported to date.

３．研究の方法

To this end, I have concentrated on a class of layered magnetic MOFs combining carboxylate-bridged paddlewheel-type diruthenium (II,II) complexes ([$Ru_2^{II,II}$]) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), in which the [$Ru_2^{II,II}$] units and redox-active linkers such as $TCNQ^{\bullet-}$ or $TCNQ^{2-}$ units can perform as electron donors for the realization of HGCT using high-affinity guest molecules (e.g. O_2, NO, and I_2, Figure 1). The single-crystal structures under the gas atmosphere have been measured by homemade measurement apparatus with the connection components between the gas supply equipment and single-crystal X-ray diffraction (SCXRD). Furthermore, the dynamical interaction between host framework and guest molecules has been verified via a variety of *in-situ* techniques such as magnetic measurement, IR spectroscopy, Raman spectroscopy, and powder X-ray diffraction (PXRD) measurement.

４．研究成果

成果１：

With adequate building blocks, MOFs can combine magnetic ordering and porosity. This makes MOFs a promising platform for the development of stimuli-responsive materials that show drastically different magnetic properties depending on the presence or absence of guest molecules within their pores. Here we report a CO_2-responsive magnetic MOF, $[\{Ru_2(F_3PhCO_2)_4\}_2TCNQ(OEt)_2]$ ($F_3PhCO_2^-$, 2,4,6-trifluorobenzoate; $TCNQ(OEt)_2$ = 2,5-diethoxy7,7,8,8-tetracyanoquinodimethane), that converts from ferrimagnetic to paramagnetic on CO_2 adsorption, and returns to the ferrimagnetic state on CO_2 desorption (Figure 2). [7] The ferrimagnetic material is a layered MOF with a $[D^+–A^–D]$ formula (Figure 2), produced from the reaction of trifluorobenzoate-bridged paddlewheel-type diruthenium(II) clusters as the electron donor (D) with diethoxytetracyanoquinodimethane as the electron acceptor (A) (inset of Figure 2). On CO_2 uptake, it undergoes an in-plane electron transfer and a structural transition to adopt a [D–A–D] paramagnetic form (Figure 2). This magnetic phase change, and the accompanying modifications to the electronic conductivity and permittivity of the MOF, are electronically stabilized by the guest CO_2 molecules accommodated in the framework.

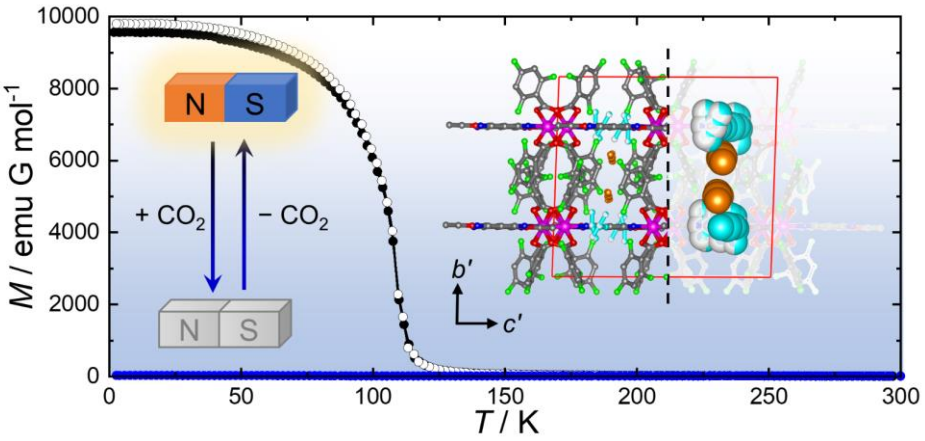

Figure 2. Field-cooled magnetization curves at H_{dc} = 100 Oe of the CO_2-responsive magnetic MOF within (blue) and without (black) CO_2 in their pores; inset: crystal structure of the magnetic MOF within CO_2.

成果２：

Changing nonmagnetic materials to spontaneous magnets is an alchemy-inspiring concept in materials science; however, it is not impossible. Here, we demonstrate chemical modification from a nonmagnet to a bulk magnet of either a ferrimagnet or antiferromagnet, depending on the adsorbed guest molecule, in an electronic-state-flexible layered MOF, $[\{Ru_2(2,4\text{-}F_2PhCO_2)_4\}_2TCNQ(OEt)_2]$ (**1**; 2,4-$F_2PhCO_2^-$ = 2,4-difluorobenzoate; $TCNQ(OEt)_2$ = 2,5-diethoxy7,7,8,8-tetracyanoquinodimethane) (Figure 3a). [8] The guest-free paramagnet **1** undergoes a thermally driven intralattice electron transfer involving a structural transition at 380 K. This charge modification can also be implemented by guest accommodations at room temperature; **1** adsorbs several organic molecules, such as benzene (PhH), pxylene (PX), 1,2-dichloroethane (DCE), dichloromethane (DCM), and carbon disulfide (CS_2), forming **1-solv** with intact crystallinity. This induces an intralattice electron transfer to produce a ferrimagnetically ordered magnetic layer (Figure 3b). According to the interlayer environment tuned by the corresponding guest molecule, the magnetic phase is consequently altered to a ferrimagnet for the guests PhH, PX, DCE, and DCM or an antiferromagnet for CS_2 (Figure 3b). This shows the first demonstration of the postsynthesis of bulk magnets using guest-molecule accommodations.

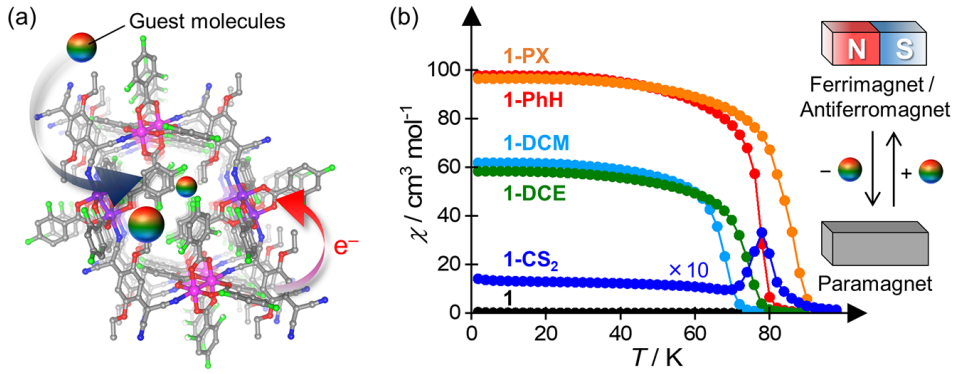

Figure 3. (a) Crystal structure of paramagnetic compound **1**. (b) Temperature dependence of χ measured at 100 Oe of **1** (black), **1-CS₂** (blue), **1-DCE** (green), **1-DCM** (cyan), **1-PhH** (red), and **1-PX** (orange).

成果 3：

Host–guest electron transfer (HGET) in molecular framework systems, such as MOFs, is a critical trigger for implementing drastic changes in both the host framework and the guest, and can enable possible modulation of the electronic and magnetic properties of frameworks. Post-synthetic incorporation of redox-active guests into redox-active MOFs is a fascinating strategy for achieving guest-driven reversible HGET. However, demonstrating a reversible phase change related to magnetic and electronic long-range ordering remains incredibly challenging. In this study, an HGET-induced magnetic phase change was determined in a porous magnetic layered MOF, $[\{Ru_2(2,6\text{-}F_2PhCO_2)_4\}_2(BTDA\text{-}TCNQ)]$ (**2**), where $2,6\text{-}F_2PhCO_2^-$ and BTDA-TCNQ represent 2,6-difluorobenzoate and bis[1,2,5]dithiazolotetracyanoquinodimethane, respectively. [9] The guest-free form **2** with an antiferromagnetic ground state transformed into a paramagnet, $[\{Ru_2(2,6\text{-}F_2PhCO_2)_4\}_2(BTDA\text{-}TCNQ)]I_3$ (**2-I₃**), by adsorbing iodine (I_2) (Figure 4). The local charge distribution of $[\{Ru_2^{II,III}\}^+\text{–}(BTDA\text{-}TCNQ)^{\bullet-}\text{–}\{Ru_2^{II,II}\}]$ in **2** was modified to $[\{Ru_2^{II,III}\}^+\text{–}(BTDA\text{-}TCNQ)^0\text{–}\{Ru_2^{II,II}\}](I_3^-)$ in **2-I₃** through HGET, according to the following route: $BTDA\text{-}TCNQ^{\bullet-} + 3/2(I_2) \rightarrow BTDA\text{-}TCNQ^0 + I_3^-$. This change was reversible via crystal-to-crystal transformation induced by heating **2-I₃**. Theoretical calculations based on structural data of **2-I₃** indicated a partial charge delocalization as $[\{Ru_2\}^{(1-\delta)+}\text{–}(BTDA\text{-}TCNQ)^0\text{–}\{Ru_2\}^{\delta+}](I_3^-)$ with $\delta \approx 0.2$, aided by weak ferromagnetic coupling. Notably, **2-I₃** exhibited a hundred-fold enhancement in electrical conductivity compared to that of **2**, indicating hopping electronic transport via inter-valence $[Ru_2]^{(1-\delta)+}$ and $[Ru_2]^{\delta+}$ units. The regulation of magnetism and electrical conductivity via HGET, which was demonstrated for the first time in this study, can facilitate the design of new porous magnets.

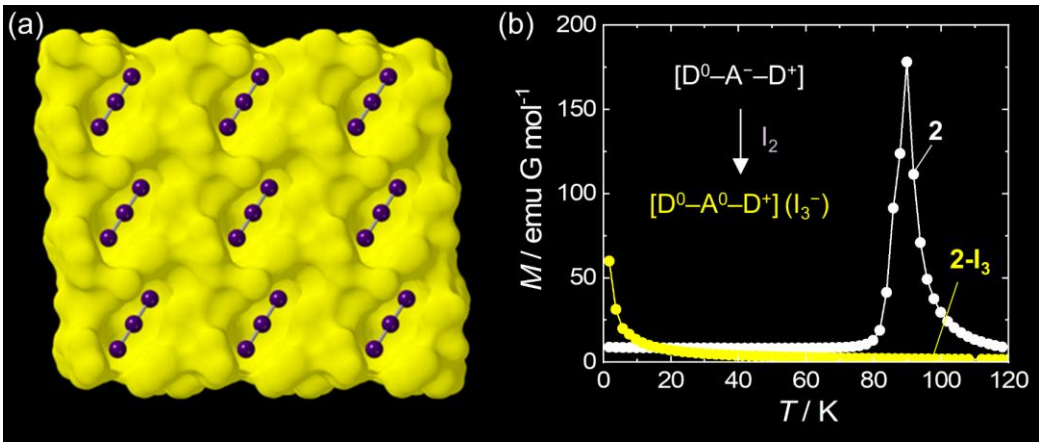

Figure 4. (a) Connolly surface diagram of **2-I₃**. (b) Field-cooled magnetization curves at H_{dc} = 100 Oe of **2** (white) and **2-I₃** (yellow).

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５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　3件／うちオープンアクセス　0件）

１．著者名 Jun Zhang, Wataru Kosaka, Yasutaka Kitagawa, Hitoshi Miyasaka	４．巻 13
２．論文標題 A metal-organic framework that exhibits CO2-induced transitions between paramagnetism and ferrimagnetism	５．発行年 2021年
３．雑誌名 Nature Chemistry	６．最初と最後の頁 191～199
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41557-020-00577-y	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Zhang Jun、Kosaka Wataru、Sato Hiroyasu、Miyasaka Hitoshi	４．巻 143
２．論文標題 Magnet Creation by Guest Insertion into a Paramagnetic Charge-Flexible Layered Metal?Organic Framework	５．発行年 2021年
３．雑誌名 Journal of the American Chemical Society	６．最初と最後の頁 7021～7031
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/jacs.1c01537	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Zhang Jun、Kosaka Wataru、Kitagawa Yasutaka、Miyasaka Hitoshi	４．巻 61
２．論文標題 A Host-Guest Electron Transfer Mechanism for Magnetic and Electronic Modifications in a Redox-Active Metal-Organic Framework	５．発行年 2022年
３．雑誌名 Angewandte Chemie International Edition	６．最初と最後の頁 e202115976
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/anie.202115976	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計3件（うち招待講演　1件／うち国際学会　1件）

１．発表者名 Jun Zhang
２．発表標題 Electronic State Modulation of Magnetic Sponge upon Solvents and Gases
３．学会等名 日本化学会第100春季年会;Asian International Symposium - Inorganic Chemistry / Coordination Chemistry and Organometallic Chemistry（招待講演）
４．発表年 2020年

１．発表者名
Jun Zhang

２．発表標題
CO2-induced Magnetic Phase Transitions between Paramagnet and Ferrimagnet in a Porous Magnet

３．学会等名
The 5th Symposium for The Core Research Clusters for Materials Science and Spintronics, and the 4th Symposium on International Joint Graduate Program in Materials Science

４．発表年
2021年

１．発表者名
Jun Zhang, Wataru Kosaka, Hiroyasu Sato, Hitoshi Miyasaka.

２．発表標題
Temperature- and Guest-Driven Electronic State Modulation in Molecular Magnets

３．学会等名
The 1st Asian Conference on Molecular Magnetism（国際学会）

４．発表年
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〔図書〕　計0件

〔産業財産権〕

〔その他〕
二酸化炭素の吸脱着による磁石のON-OFF制御に成功ー”二酸化炭素磁気センサー”への道筋
http://www.tohoku.ac.jp/japanese/2020/12/press20201201-01-mof.html
分子の吸着で磁石を創る 吸着分子に依存した磁気相変換の実現
https://www.tohoku.ac.jp/japanese/2021/04/post-62.html
ホストーゲスト間電子移動の制御による磁石スイッチ 新たな電子状態変換機構に基づく磁気相変換に成功
https://www.tohoku.ac.jp/japanese/2022/03/press20220315-04-Transfar.html

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関